

Silicon Carbide Coating on Graphite and Isotropic C/C Composite by Chemical Vapour Reaction

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Abstract

The application of Carbon and graphite based materials in unprotected environment is limited to a temperature of 450°C or so because of their susceptibility to oxidation at this temperature and higher. To overcome these obstacles a low cost chemical vapour reaction process (CVR) was developed to give crystalline and high purity SiC coating on graphite and isotropic C/C composite. CVR is most effective carbothermal reduction method for conversion of a few micron of carbon layer to SiC. In the CVR method, a SiC conversion layer is formed by reaction between carbon and gaseous reagent silicon monoxide at high temperature. Characterization of SiC coating was carried out using SEM. The other properties studied were hardness density and conversion efficiency.

Keywords : Carbothermal reduction, Graphite, Silicon carbide, Chemical vapor reaction

1. Introduction

Graphite exhibits high strength at high temperatures, high thermal conductivity and low thermal expansion whereas carbon-carbon composites add to the fracture toughness. Therefore carbon-carbon composites are widely used in aerospace industries like brake disk, nose tips and engine components, heat exchanger, diesel engine components, refractory material, hot press die components, crucible etc. [1]. However, in oxidative environment, carbon-carbon composites get oxidized at 450°C. Therefore the need exists to give oxidation protection coatings on to carbon-carbon composite and graphite materials for their application at high temperature. Since these coatings should be compatible with base carbon materials, SiC has been established to be the best solution as oxidation protection coating [1, 2]. Various

methods used for production of SiC are CVD, CVI, polymer pyrolysis, reaction bonding, sol-gel etc. [3-7]. However, high manufacturing cost and limited applicability of these techniques restricted their application to high-tech products only. In order to give SiC coating to general engineering products, a low cost chemical vapour reaction process has been developed for giving high thermally stable crystalline SiC coating on graphite and C/C composite products [8-10].

The CVR method is based on carbothermal reduction in which SiC forms as result of reaction between silicon oxide and carbon as illustrated in Fig. 1. Carbon substrate is taken in solid form whereas silicon oxide is generated in vapour form as result of reaction between silica and silicon. CVR method has been used to develop SiC fibers and SiC-SiC composite from carbon fiber, graphite as well as carbon-carbon composite [10, 11]. In the present work this techni-

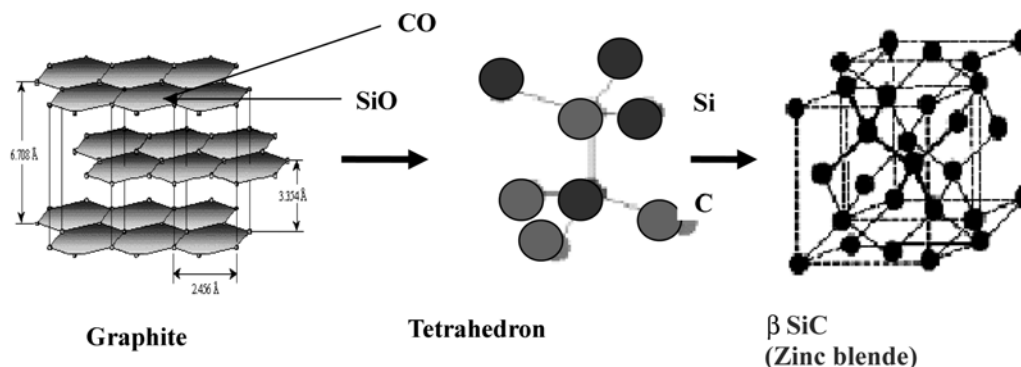


Fig. 1. Schematic illustration on transformation of graphite into β SiC.

que has been used to give SiC coatings on to various carbon and graphite substrates including C/C composites. Characterization of SiC coating was carried out using SEM and by evaluating its physical properties and hardness etc., while thermal stability was studied using TGA.

2. Experimental

Silica powder and silicon metal powder were mixed in stoichiometric ratio (2.54:1 w/w) using ball mill for 17 hrs. Carbon substrate to be coated (Isotropic C/C composite heat treated to 1000°C and graphite) were taken in a ceramic crucible filled with silica and silicon powder mixture and covered with graphite plate. The reaction was carried out in alumina tube furnace in argon atmosphere at 1500-1600°C for different times.

3. Characterization

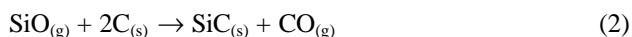
The uniformity of the coating on a standard small samples (5 mm×5 mm×5mm) and surface morphology was observed using scanning electron microscope (HITACHI S3000N). Formation of SiC was confirmed by XRD using. Open porosity was measured by kerosene impregnation method while hardness measurement was carried out using Rockwell hardness tester. Thermal stability and percentage conversion of carbon to silicon carbide was determined by Thermo-gravimetric analysis in air using Mettler TG50.

4. Results and Discussion

CVR reaction is based on carbothermal reduction. The carbothermal reduction can be described by following reactions.

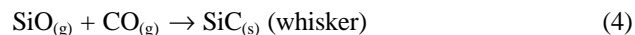
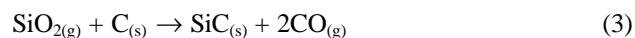


During first stage, the silicon reacts with silica leading to the formation of silicon monoxide.



In second stage, gaseous silicon monoxide reacts with carbon substrate and resultant product SiC is formed. However, if the reaction is not controlled and the parameters are not optimized, SiC whiskers and SiC particles are formed on the

carbon substrate following reactions (3) and (4) along with unreacted silicon and silica mixture.



4.1. Physical characteristics of the Materials before and after coating

Table 1 shows the physical characteristics of the samples before and after CVR coating. As seen from the table, density of both the samples increased after SiC coating. This is because SiC has higher density than carbon. Similarly, the porosity of the samples also decreased after the coating. Moreover, it is found that the effect is more pronounced for isotropic C/C composites as compared to graphite. This also means that amorphous carbons are more reactive with silicon oxide as compared to crystalline graphite.

4.2. SEM studies

Samples were examined under SEM before and after the reaction. Figure 2(a, b) show SEM photographs of SiC coated graphite samples and (c, d) are of isotropic C/C composites. These exhibit smooth conversion of carbon to SiC. Grain size of SiC coated surface of isotropic C/C composite has been observed to be smaller as compared to SiC coated Graphite at 1550°C/7 hrs. Latter also exhibit formation of whiskers of SiC on to the coated graphite surface. Formation of cracks is also observed. However, the crack formation is much more on SiC coated graphite as compared to SiC coated isotropic C/C composite. It is due to the mismatch of CTE of SiC and graphite while in case of isotropic carbon the CTE of SiC is nearly same to that of the isotropic carbon/carbon composites.

4.3. XRD analysis

Fig. 3(a, b) Show XRD patterns of the coated samples. These are of bulk material and hence will give XRD peaks corresponding to base carbon as well as of the SiC coating. These could also be used as indication of the extent of conversion of carbon to SiC in bulk samples. The XRD patterns of both the samples exhibit peaks at 26° & 54° due to graphite and at 35.5° and 60° and 72° due to SiC. Therefore, both materials after reaction show the presence of polycrystalline β-SiC as well as carbon. In the composites,

Table 1. Physical characteristics of SiC coated graphite and isotropic carbon/carbon composite coated at 1550°C for 7 hrs

Substrates	Density before CVR (gm/cc)	Density after CVR (gm/cc)	Porosity before CVR (%)	Porosity after CVR (%)	Hardness before CVR HRL	Hardness after CVR HRL
Graphite	1.79	1.829	16.96	13.36	87.15	92.4
Iso. C/C composite	1.29	1.437	28.91	22.37	74.95	81.85

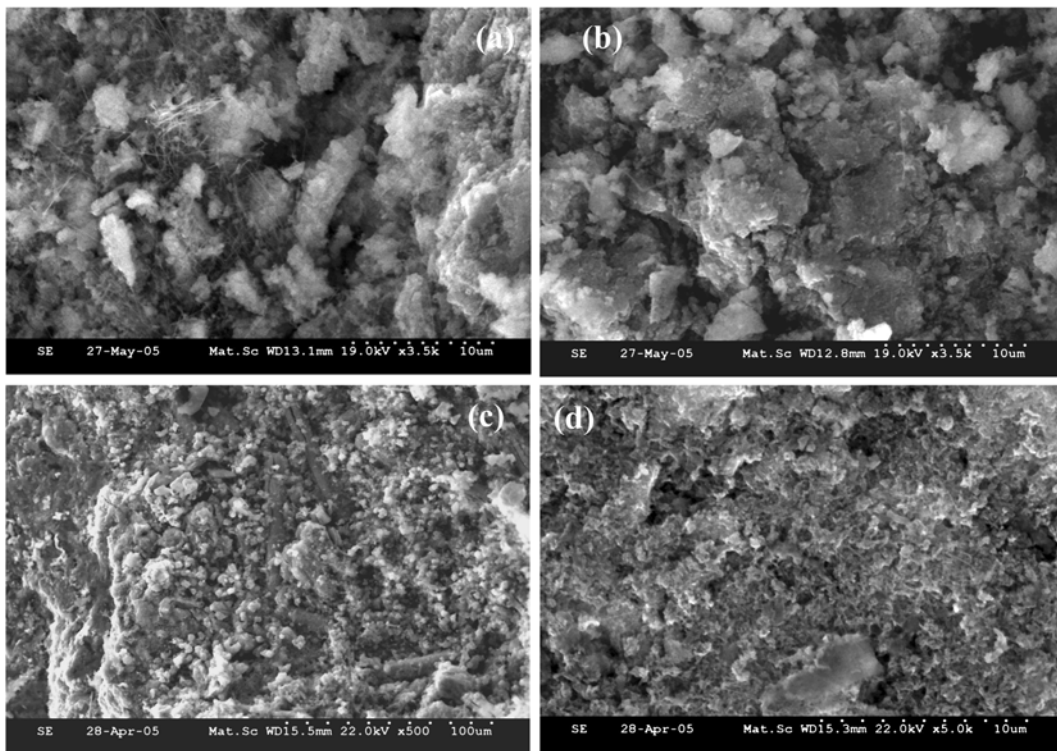


Fig. 2. SEM photographs of SiC coated graphite substrates (a, b) and SiC coated isotropic C/C composite (c, d).

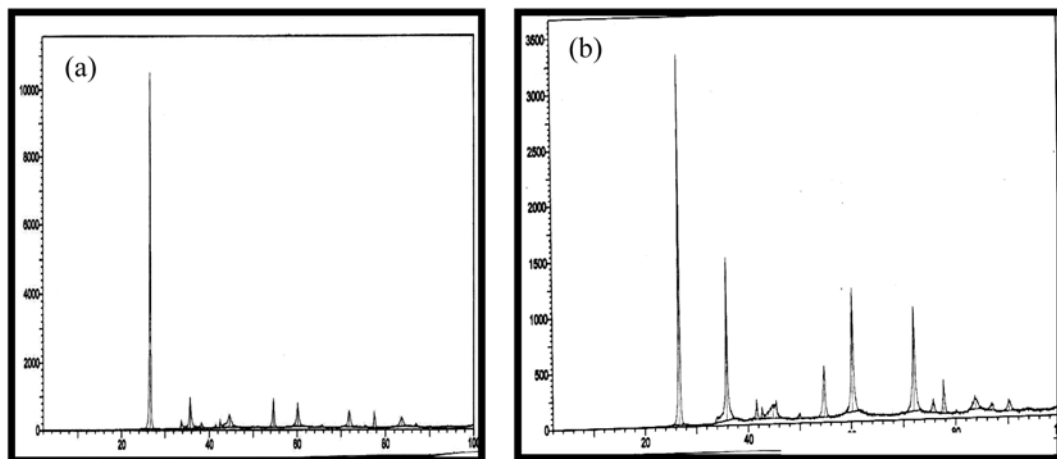


Fig 3. XRD pattern of (a) high density graphite and (b) low density carbon/carbon composites.

the carbon peak is due to the carbon fibers which exhibit sharp peak. As seen from XRD pattern, low density carbon/carbon composites samples after reaction exhibit lower peak height for carbon as compared to high-density graphite based samples. This supports the observation made above that conversion to SiC is higher for low density less graphitic carbon/carbon composites.

4.4. Studies on Oxidation resistance of coated samples as determined by their thermal stability in air

Fig. 4 is the thermogravimetric analysis in air of the coated graphite (HG) and C/C composites (C/C) samples. Carbon and graphite start getting oxidized at 450°C. However, as seen from the Fig. 4, oxidation of the coated samples start at temperature more than 700°C. Again, the weight loss of coated C/C composites starts at higher temperature as compared to that of coated high density graphite. This also confirms that the reactivity of C/C composites is higher than that of pure graphite. TGA technique was also used to determine percentage conversion

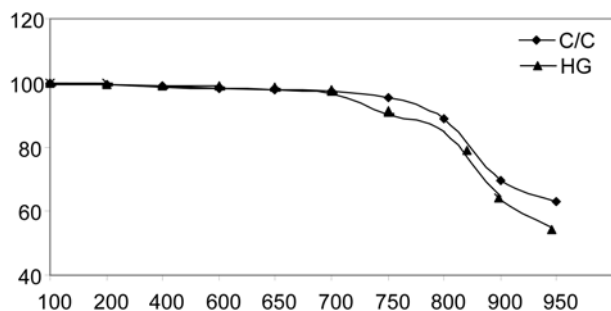


Fig. 4. Thermogravimetric analysis in air of the coated samples.

Table 2. Conversion of carbon to SiC

Sample code	Reaction condition	Substrate material	% Conversion to SiC
HG	1550°C/7 hrs	High density graphite	49.4
C/C	1550°C/7 hrs	Carbonized Carbon/Carbon composites	62.9

Table 3. Hardness of the coated samples

Substrates	Density before CVR	Density after CVR	Hardness before CVR	Hardness after CVR
	(gm/cc)	(gm/cc)	HRL	HRL
Graphite	1.79	1.829	87.15	92.4
Iso. C/C composite	1.29	1.437	74.95	81.85

of carbon to SiC in both the samples. The findings are compiled in Table 2.

4.5. Measurement on Hardness of the samples

SiC is much harder than carbon or graphite. The hardness results on the coated composites are compiled in Table 3. As seen from the table, the hardness of the samples also increase after coating. This is due to the hardness of SiC. Lower hardness of the Carbon/carbon composites is due to the porous nature of the composites. However, after coating, the C/C composites exhibit more increase in hardness as compared to graphite. This again is attributed to higher conversion of Carbon/Carbon composites to SiC.

5. Conclusions

The SiO vapour generated from reaction between silica and silicon is active to react with different type of carbon substrates. The extent of conversion of carbon to SiC greatly depends on the nature of host carbon and its microstructure. Highly graphitic materials exhibit lower conversion as compared to isotropic carbon materials. SiC coating enhances the oxidation resistance as well as hardness of the host carbon materials.

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